Ordering of TiO_2 nanoparticles to mesoporous structures using self-synthesized acrylamide-styrene block copolymers

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Introduction

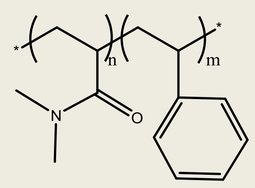
Mesoporous, crystalline metal oxides are rapidly gaining importance for applications in sensors, (photo)catalysis and energy generation/storage. For most applications, the ideal material should be **crystalline** as well as **porous**, enhancing surface related phenomena. The commonly used synthetic procedures involve the creation of an amorphous network from sol-gel precursors templated by organic surfactants. This requires crystallization at elevated temperatures, which often results in a collapse of the mesostructure, because the surfactant generally degrades before TiO_2 crystallization. Hence, specific surfaces > 250 m^2/g are only reported for largely inefficient amorphous materials processed at reduced temperatures.(1)

Two approaches will be investigated to tackle the trade-off between crystallinity and increased surface. The first encompasses the application **thermally stable block copolymers**, used as pore formers, suppressing shrinkage and collapse of the mesoporous structure during crystallization at elevated. With this sol-gel approach a **surfactant** is mixed with a **Ti^{4+}- precursor** (Ti-isopropoxide and HCl) that hydrolyses and condenses around the supramolecular structure formed by the surfactant. In a next step the surfactant is removed by a **thermal procedure** which also **crystallizes the titania** (+ 400 °C). The second strategy consists of the **ordering of previously synthesized nanocrystals to porous structures**. Here **nanocrystals** are ordered into a porous structure with **suitable surfactant molecules**. This will lead to an important reduction of the processing temperatures: a **mild temperature treatment** is sufficient **to connect the particles** and remove the template. For the two approaches the TiO_2 powders are formed via EISA (Evaporation Induced Self-Assembly) at 60°C. Finally, a thermal treatment is performed: 2h at 450 °C, 2°C/min.

Block copolymer

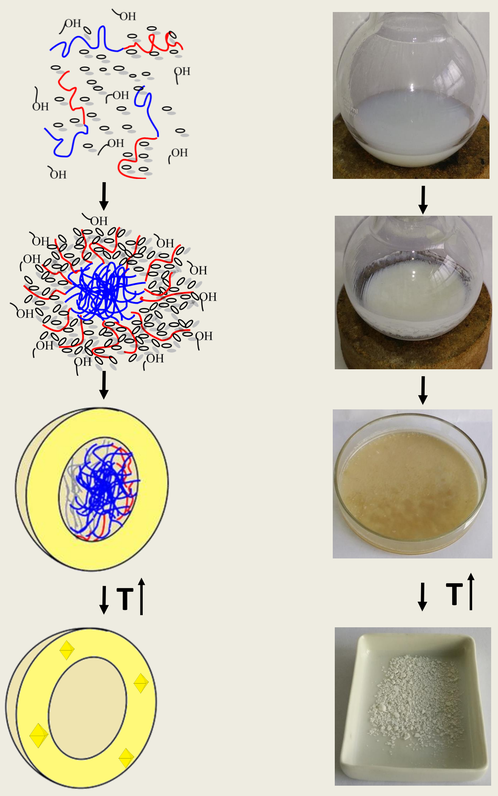
PDMA-b-PS (Poly(dimethylacrylamide)-block-polystyrene):

- Via Reversible Addition Fragmentation chainTransfer (RAFT)

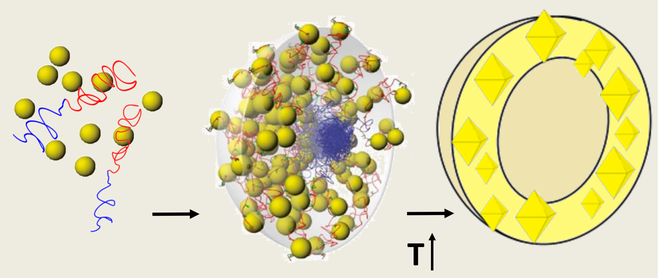


Polymer	PDMA (g/mol)	PS (g/mol)	PDI
PDMA-PS_{4k}	5000	4000	1.2
PDMA-PS_{5k}	5000	5000	1.26
PDMA-$PS_{7,5k}$	5000	7500	1.16
PDMA-PS_{9k}	5000	9000	1.18

Sol-gel approach

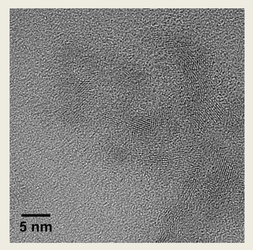


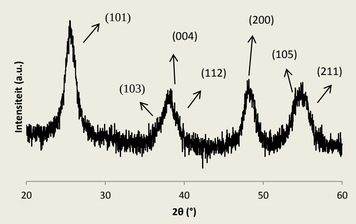
Nanocrystal soft-templating approach



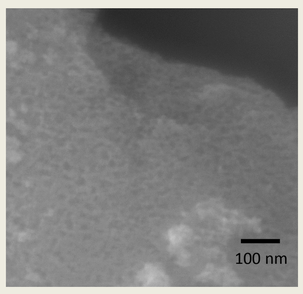
Ultrasmall spherical nanoparticles are used:

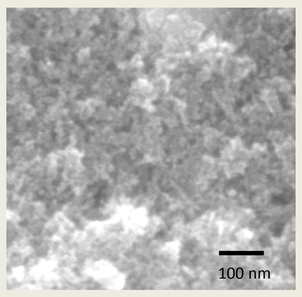
- Microwave synthesis with *tert*-BuOH, toluene and $TiCl_4$ (2)
- Suspendable in EtOH





Porous and crystalline powders





Sol-gel approach: BET surface area (m^2/g)	Polymer	Nanocrystal approach: BET surface area (m^2/g)
241	PDMA-PS_{4k}	270
211	PDMA-PS_{5k}	/
192	PDMA-$PS_{7,5k}$	(97)
215	PDMA-PS_{9k}	(88)

Conclusions

These preliminary results show that the current state-of-the-art for mesoporous and crystalline TiO_2 (250 m^2/g) can be reached using the self-synthesized PDMA-b-PS block copolymers. Nevertheless, much progress can still be made by varying the concentrations of polymers and Ti-precursor, adapting the temperature and moisture levels of the EISA-process and optimization of the thermal treatment. The nanocrystal route leaded to less satisfactory results, but only a few tests with unstable solutions were performed, where the block copolymer or the nanocrystals precipitated except for PDMA-PS_{4k}. Furthermore it will be investigated if a lower thermal treatment temperature (f.e. 375 °C) will lead to higher surface areas, as less of the mesoporous structure will collaps.

References

1. Meynen V and Cool P, Microporous and Mesoporous Materials, 2009, **125**, 170.
2. Szeifert JM and Feckl JM, Journal of the American Chemical Society, 2010, **132**, 12605

Acknowledgement

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